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Highly Ordered Thin Films of Polyheterocycles: A Synchrotron Radiation
Study of Polypyrrole and Polythiophene Langmuir-Blodgett Films

by

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HIGHLY ORDERED THIN FILMS OF POLYHETEROCYCLES: A SYNCHRONTRON RADIATION STUDY
OF POLYPYRROLE AND POLYTHIOPHENE LANGMUIR-BLODGETT FILMS

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ABSTRACT

Langmuir-Blodgett films have been made with 3-n-hexadecylpyrrole and 3-n-octadecylpyrrole monomers and copolymers with unsubstituted pyrrole made by chemical polymerization at the air-water interface on a subphase containing FeCl_3 . Langmuir-Blodgett films consisting of mixtures of stearic acid and alkylsubstituted polythiophenes have also been made as bilayer films. The orientation of single and multilayer films on platinum substrates have been studied by Near Edge X-ray Absorption Fine Structure Spectroscopy which also gives information about charge transfer interactions between the aromatic groups and the metallic substrates. The alkylsubstituted pyrroles form highly ordered two-dimensional structures. FeCl_3 initiated copolymerization with unsubstituted pyrrole leads to a more disorderd system. In the case of polythiophene-stearic acid bilayers, the stearic acid layers are highly ordered. The poly(alkyl thiophene) layers sandwiched between stearic acid layers, on the other hand, exhibit random orientation of the thiophene moieties.

*Ube Industries Fellowship Recipient

The Langmuir-Blodgett (LB) technique can be used to deposit ultrathin (~ 25 Å) organic and organometallic films on solid surfaces. Highly two-dimensionally ordered monolayer and multilayer structures can be assembled. The rapidly increasing interest in LB films arises from their potential application in a number of thin film technologies such as nonlinear optics, microlithography and biochemical sensing, where highly ordered and anisotropic structures can result in unique properties and high sensitivity. In the case of conducting polymers, the assembling of LB structures may allow studies of the intrinsic anisotropy of the electronic properties of the materials.

Detailed characterization of the molecular structure of the films is essential for developing efficient techniques for system design. A multitude of techniques have been adapted to study the orientational behavior of LB films, including infrared [1,2], Raman [3], electron diffraction [4], and x-ray diffraction [5]. The studies have been performed on multilayer films, since nondestructive techniques to study monolayers are still scarce. Recently, the technique of Near Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) has been applied to the study of classical monolayer LB films of arachidic acid and cadmium and calcium arachidate [6,7].

NEXAFS is a powerful technique for investigating structural and electronic properties of thin organic films on surfaces. It is essentially a nondestructive technique based on synchrotron radiation and has been shown to be useful for studying the orientational behavior and bonding of organic molecules [8,9] and thin polythiophene films [10] on metallic substrates.

In the NEXAFS technique, core level electrons are excited to unoccupied orbitals near the ionization threshold. In this study we are concerned with excitations from the carbon $1s$ and sulfur $2p_{3/2}$ and $2p_{1/2}$ levels to unoccupied π^* and σ^* orbitals. The strength of the excitation is monitored via the core-hole decay which is dominated by Auger processes. By scanning the incident photon energy and monitoring the Auger electrons, the presence of π^* and σ^* orbitals and their orientation relative to the surface can be determined. The possibility of studying the orientational behavior of molecular groups drives from the high degree of polarization of the incident photon beam emanating from a synchrotron. In the dipole approximation, the resonance peaks corresponding to transitions to empty π^* and σ^* orbitals will have a maximum intensity when the electric field vector is parallel to the π and σ orbitals, respectively [11]. Varying the angle between the electric field vector and the orbital in question will allow a measurement of the orientation of the molecular group which contain the orbital.

The NEXAFS study was performed on beam line U-14 at the National Synchrotron Light Source. The spectra were obtained by total electron yield measurement of the sample current.

EXPERIMENTAL RESULTS AND DISCUSSION

The types of LB film structures which are considered in this paper are: (1) molecular layers of 3-alkyl substituted pyrrole, (2) copolymers between 3-alkyl pyrrole and unsubstituted pyrrole; (3) bilayers formed by mixtures of stearic acid and prepolymerized and soluble poly(alkyl thiophenes). Cases (2) and (3) are illustrated schematically in Fig. 1.

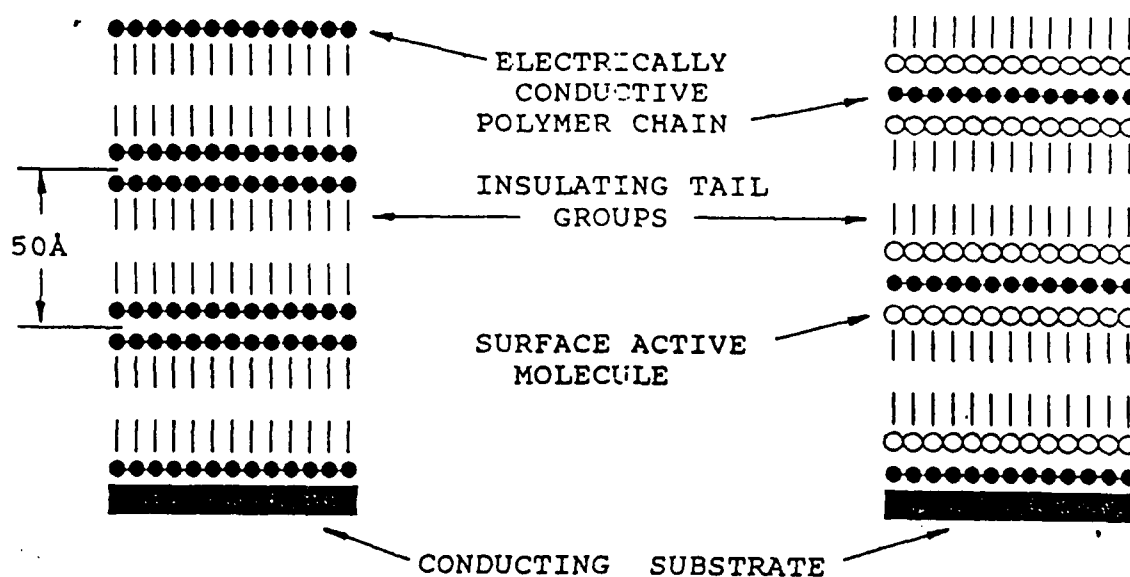


Fig. 1. Schematic illustration of highly anisotropic two-dimensional LB structures of conducting polymers.

LB Films of Alkylpyrrole

3-hexadecylpyrrole (HDP) and 3-octadecylpyrrole (ODP) monomers were synthesized according to procedures described elsewhere [12,13]. All LB films were prepared on Lauda film balances. The monolayers were spread from chloroform solutions. Details of the film preparations are presented elsewhere in these proceedings [14]. Figure 2(a) shows the carbon K-edge NEXAFS spectrum of a monolayer ODP monomer film on a Pt substrate with light incident normal to the substrate and at grazing incident angle (20°). In the first case the electric field vector is parallel to the substrate, and in the second case the electric field vector is close to normal to the substrate. The energies and proposed assignment of the features are listed in Table 1.

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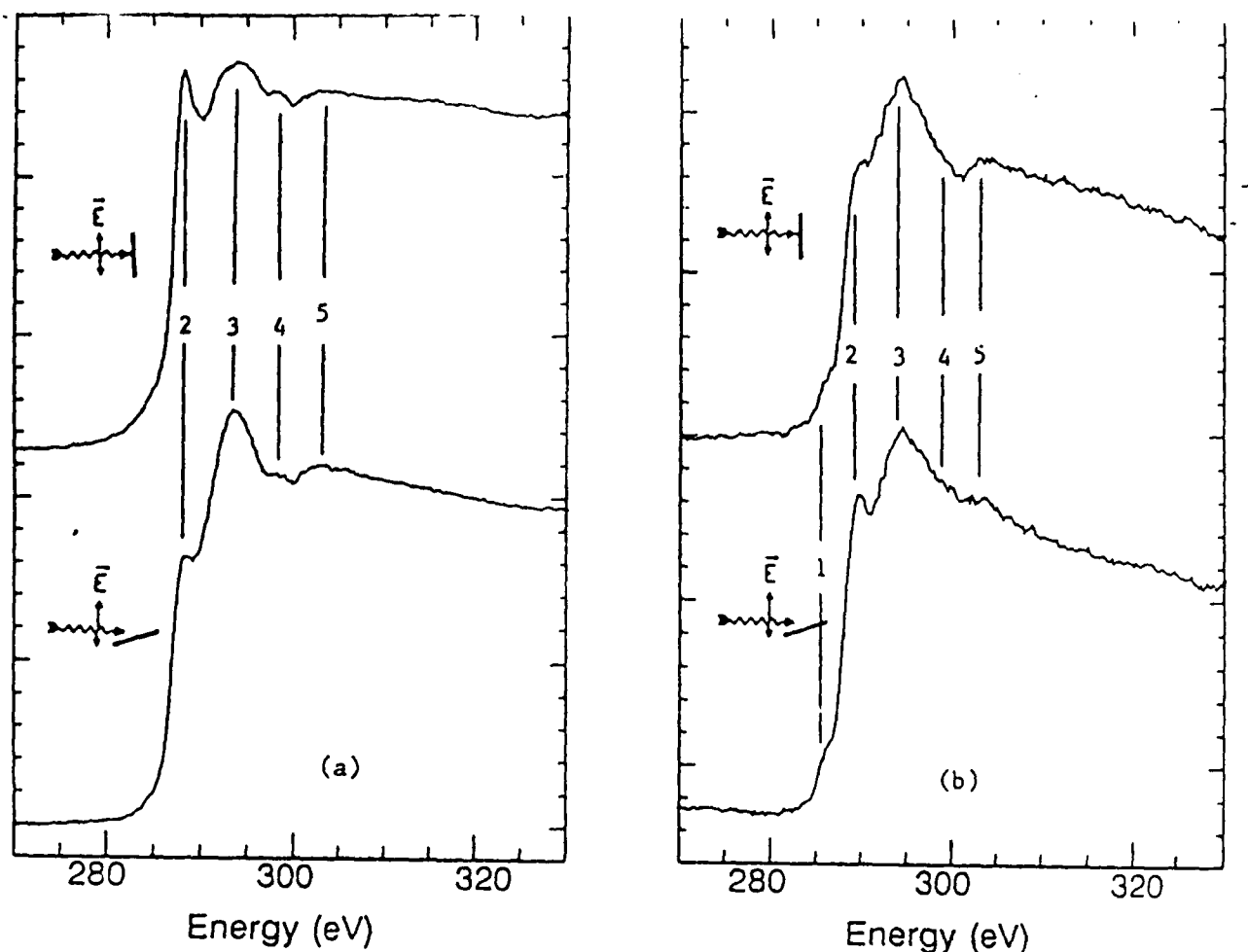


Fig. 2. Carbon K-edge NEXAFS spectra of single layer ODP monomer film (a) and single layer copolymer film with unsubstituted pyrrole (b) on platinum.

TABLE 1

Energies and assignments of features in the carbon 1s spectrum of octadecylpyrrole LB film.

No.	ODP Monolayer E(eV)	Assignment	
		Ring	Hydrocarbon chain
1	285.5	π^* $3b_1$ (C=C)	
2	288.5	$[\pi^* 2a_2$ (C=C)]	π^* (CH ₂)
3	294	σ^* (C-C)	σ^* (C-C)
4	298.5	σ^* (C-C)	σ^* (C-C)
5	303	σ^* (C=C)	

As can be seen from Fig. 2a, there is a pronounced polarization dependence of the spectral features in the near-edge region. Since most of the carbon atoms are in the hydrocarbon chain, the carbon spectrum will be dominated by the chain. The strong polarization dependence of the spectrum implies that the chains are highly ordered. The feature labeled (2) corresponds to excitation to an empty orbital associated with the C-H bonds on the chain. This orbital

4

5
is perpendicular to the chain direction, and its associated feature is most pronounced with the electric field vector parallel to the substrate. The feature labeled (3) is associated with the C-C bond which, on average, is along the chain direction. This feature is most pronounced with the electric field vector normal to the substrate. We can, therefore, conclude that the chains are oriented at an angle which approaches the normal to the substrate. 4

The tilting from the normal is most likely due to interaction between the π -electron structure of the pyrrole ring and the Pt surface. When similar spectra are analyzed for multilayer films, the chains are found to be oriented essentially normal to the substrate from the second layer and upwards [2].

Copolymers of ODP and unsubstituted pyrrole can be formed at the air-water interface by dropping a chloroform solution of pyrrole and ODP onto a water subphase which contains FeCl_3 . An excess of unsubstituted pyrrole is needed to account for the solubility of pyrrole in water [14]. Figure 2(b) shows the carbon 1s spectra of a single layer of pyrrole/ODP copolymer on platinum. As can be seen from the figure, there is less polarization dependence which indicates either a higher degree of disorder or a tilting of the chains at an angle which approach 45° .

A second feature which is not apparent in the monomer film (Fig. 2a) is labeled (1) in Fig. 2b and corresponds to a π^* orbital associated with the delocalized π -electron structure of the pyrrole ring. When heterocycles are in intimate contact with a metal surface, charge transfer to the metal occurs, resulting in strong bonding or catalytic decomposition [9,15]. The strong interaction with the metal substrate results in a shift of the spectral feature and it is no longer apparent in a spectrum dominated by the hydrocarbon chains.

In the copolymer film the pyrrole head groups may not be in intimate contact with the metal substrate. The oxidized film contains anions, which are derived from the FeCl_3 in solution. Since the anions are water soluble, their most likely position would be underneath the compact alkylpyrrole film at the air-water interface. Subsequent to transfer, their most likely position would be between the pyrrole head groups and the metal substrate. This could lead to a separation of the pyrrole moieties from the metal substrate and prevent the strong interaction which occurs with intimate contact. The transition to the unaltered π^* orbital is consequently observed. This function is also apparent in the spectra of multilayer monomer films since the NEXAFS technique being surface sensitive, only samples the top layers [2].

5 LB Films of Stearic Acid/Poly(alkylthiophene) Mixtures

Figure 3 shows the carbon 1s and the sulfur $2p_{3/2}$ and $2p_{1/2}$ spectra of a film consisting of ten poly(3-octyl thiophene)/stearic acid (PTSA) bilayers. The polythiophene is undoped. The energies and proposed assignment of the

6 features are given in Table 2 and Table 3. The carbon 1s spectra of fig. 3a shows clear polarization dependence, indicating a highly ordered structure with the orientation of the hydrocarbon chains approaching the normal to the substrate. The feature labeled (1) and assigned to the π -electron structure of the thiophene ring is present in the ten-layer structure. The spectrum is effectively that of the top layer as the technique is highly surface sensitive. Feature (1) is not present in single layer films, indicative of strong interaction with the Pt substrate similar to the case for pyrrole.

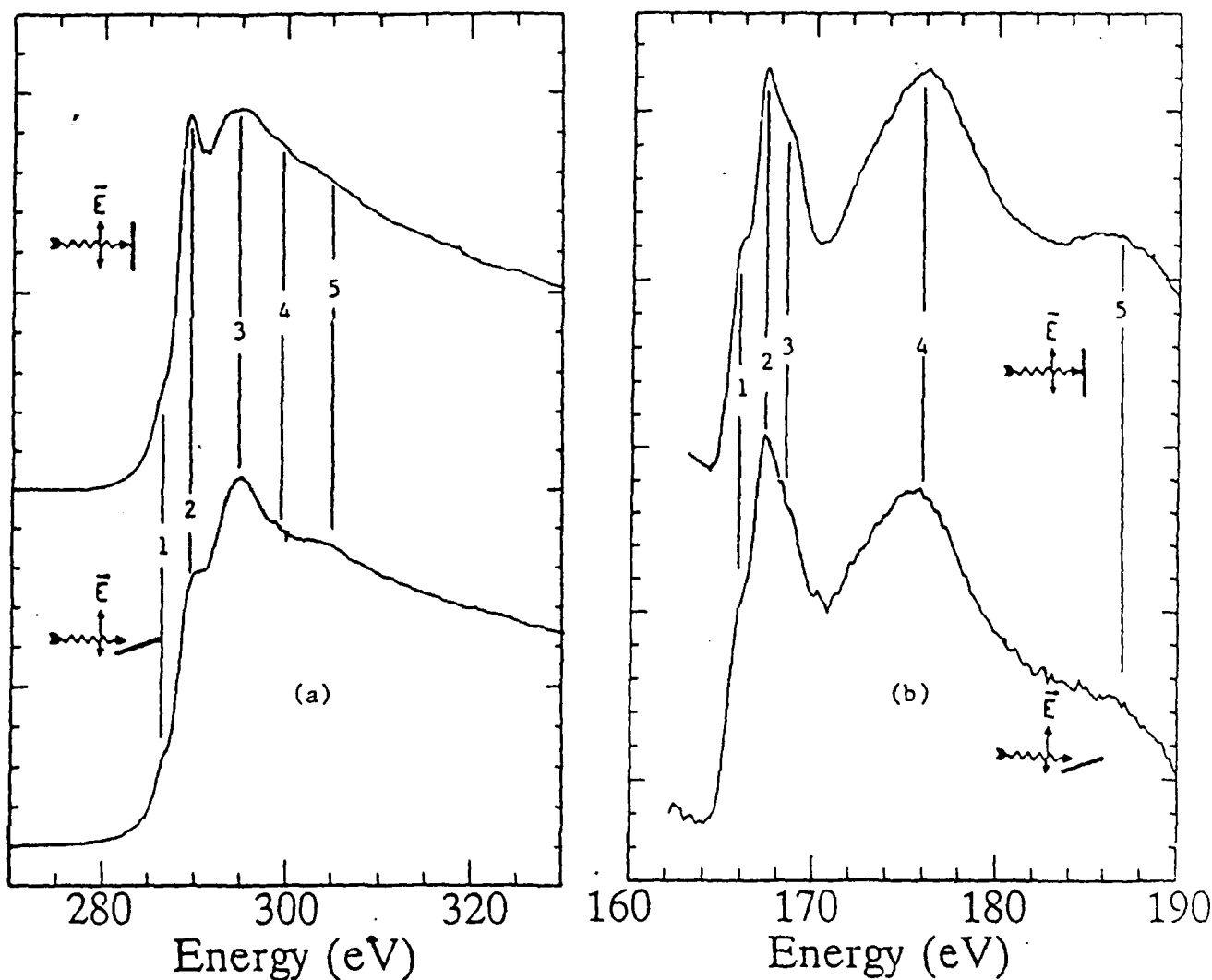


Fig. 3. Carbon K-edge (a) and sulfur L-edge (b) spectra for a ten-layer film of poly(3-octyl thiophene) and stearic acid.

The corresponding spectra for the sulfur L-shell electrons are shown in Fig. 3b. The spectra in Fig. 3b exhibit no polarization dependence. This we interpret to imply an absence of ordering of the thiophene moieties, i.e. the thiophene rings are randomly oriented in the plane defined by the stearic acid layers. That the two-dimensional ordering is intact is shown by x-ray diffraction data [14].

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TABLE 2

Energies and assignments of features in the carbon 1s spectrum of poly(3-octyl thiophene)/stearic acid LB films.

No.	PTSA 10 layers E(eV)	Assignment	
		Ring	Hydrocarbon chain
1	285.5	π^* 3b ₁ (C=C)	
2	288.5	[π^* 2a ₂ (C=C)]	π^* (CH ₂)
3	294	σ^* (C-C)	σ^* (C-C)
4	298.5	σ^* (C-C)	σ^* (C-C)
5	303	σ^* (C=C)	

TABLE 3

Energies and assignments of features in the S 2p spectrum of poly(3-octyl thiophene)/stearic acid LB films.

No.	PTSA 10 layers E(eV)	Assignment	
		3/2	1/2
1	165.5	π^* 8b ₂ (C-S)	
2	167	π^* 2a ₂	σ^* 8b ₂ (C-S)
3	168.4	σ^* 12a ₁	π^* 2a ₂
4	175.5		S 3d
5	187		S 3d

Figure 3a and 3b independently give information about the ordering of the two components of the system. The carbon 1s spectra derive primarily from the stearic acid component as that is where most of the carbon atoms reside. The sulfur spectra, on the other hand, derive exclusively from the thiophene rings. Thus, it is possible with this technique to independently study individual components of complex systems by scanning the photon energy through the absorption edges of the constituent elements.

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